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Microstructural studies of platinum nanoparticles dispersed in Nafion membrane

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The aim of this work was to prepare a nanocomposite membrane based on platinum nanoparticles dispersed onto/inside of Nafion, by *in situ* reduction of platinum precursor. Two types of the reducing agent (sodium borohydride) concentrations have been used in order to investigate the influence over platinum nanoparticles size and distribution, performering complementary microstructural analysis, e.g. High Resolution-Transmission Electron Microscopy (HR-TEM), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD).

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1. Introduction

Nafion® is a perfluorinated ion-exchange membrane with a wide variety of commercial uses, especially in proton exchange membrane (PEM) and direct methanol fuel cells, due to its outstanding chemical, mechanical and thermal stability and high proton conductivity [1–5]. The morphology of Nafion and the relationship between its structure and unique properties have not been yet clearly identified [6]. The accurate structure of Nafion has been investigated by various experimental techniques and morphological models [7]; according to the cluster-network model [8,9], there are 4–5 nm diameter clusters of sulfonated perfluoroalkyl ether groups, which are interconnected by hypothetical tiny channels of 1 nm.

Nafion membranes tend to significantly dehydrate at high temperature or low relative humidity leading to ohmic losses, low proton conductivity and poor PEMFC performance. In response to this challenge, extensive efforts have been made to improve the properties of Nafion, and they can be divided into three main categories: (*i*) modification of Nafion membrane by inclusion of inorganic additives [10, 11]; (*ii*) membranes based on sulfonated hydrocarbon backbones [12-15]; and (*iii*) acid impregnated polymer matrices [16, 17]. As response to the first category is incorporating nanometer sized of metallic particles like platinum or platinum alloys or hygroscopic metal oxides (silica, titania, and zirconia phosphate) into Nafion [18–20] to improve the hydration characteristics of Nafion. Tang et al. [21] reported that self-assembled palladium (Pd) nanoparticles on the Nafion membrane surface lower the methanol crossover rate in DMFCs. Uchida et al. [22] and Mau et al. [23] incorporated Pt into Nafion membranes using a liquid-phase impregnation - reduction method. Liu et al. [24] reported that Pt nanoparticles without a carbon support could be prepared by the alcohol reduction method using an anionic Pt complex.

The electrocatalytic activity of metal nanoparticles is strongly dependent on their composition, size, surface area and surface morphology [25]. To obtain high surface area, metal nanoparticles catalysts were usually dispersed in an organic polymer such as Nafion [26, 27], colloids [28], surfactants [29] and porous substrates, which enables metal particles to be highly dispersed and stable. In particular, platinum (Pt) nanoparticles are of great interest because of their excellent catalytic activity. Their catalytic activity depends on the size distribution and morphology of the particles and therefore, the synthesis of particles with well controlled sizes and morphology could be critical for these applications. Furthermore, the highly dispersed Pt reduced the amount of methanol crossover, leading to an increase in the cathode potential compared to that of the pristine Nafion.

The idea of this work was to prepare a nanocomposite membrane based on platinum nanoparticles (PtNPs) dispersed onto/inside of Nafion, by in situ reduction of platinum precursor, chloroplatinic acid. Sodium borohydride was used as reducing agent with two concentrations, in order to check the influence over platinum nanoparticles morphology. The final nanocomposite membranes were investigated from morphological, compositional and microstructural point of view in order to achieve the optimum method for fabrication of Pt-Nafion nanocomposite membrane where the PtNPs are uniformly distributed and could work as efficient catalyst.

2. Experimentals

2.1. Chemicals

Cloroplatinic acid, $H_2PtCl_6 \times H_2O$, sodium borohydride ($NaBH_4$), ethanol alcohol, sodium hydroxide and Nafion 117 membrane have been purchased from Sigma-Aldrich, Germany. Nafion 117 has typical thickness 7 mil (178 μm) and equivalent weight of 1,100 grams. All aqueous solutions were made with deionized water, which was further purified with a Milli-Q system (Millipore).

2.2. In situ preparation of PtNPs / Nafion nanocomposite membrane

Before starting the experiments, the Nafion membrane was protonated according to the conventional procedure, by successive heating at 80 ºC for 40 minutes in H_2O_2 3%, to eliminate the organic impurities, deionized water with 18 MΩ resistivity and H_2SO_4 9%, to eliminate the metallic impurities.

Impregnation of the protonated Nafion membrane with Pt has been realized in a two steps process: (i) firstly immersing in 10 mM H_2PtCl_6 solution for 2 hours, at 60 ºC, the pH of the solution being adjusted to 8.5 with 6M NaOH; (ii) the platinum complex cations were then reduced in the Nafion membrane by using a $NaBH_4$ solution. This procedure was schematically showed in Fig. 1:

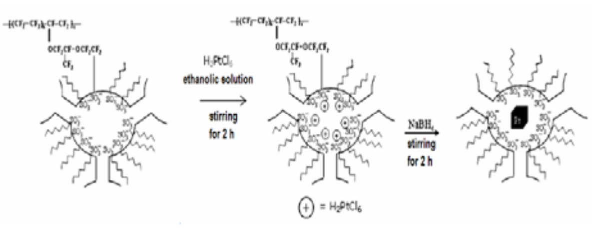

Fig. 1. The scheme for in situ preparation of PtNPs / Nafion nanocomposite membrane.

The reactions for platinum complex reductions are written down bellow:

$$H_2PtCl_6 \leftrightarrow 2H^+ + [PtCl_6]^{2-} \tag{1}$$

$$[PtCl_6]^{2-} \xleftrightarrow{+2e^-} [PtCl_4]^{2-} + 2Cl^- \tag{2}$$

$$[PtCl_4]^{2-} \leftrightarrow Pt^0 + 4Cl^- \tag{3}$$

In order to see the influence of the reducing agent, two concentration of the reducing agent were used, 25 mM and 85 mM.

3. Results and discussions

3.1. Morphological characterization and compositional analysis

The nanocomposite membrane morphology has been investigated using Field Emission Gun Scanning Electron Microscopy (FEG-SEM) *Nova NanoSEM 630* with a resolution of 1.8 nm ≅ 3 kV, and also High Resolution-Transmission Electron Microscopy (HR-TEM), TECNAI F30G^2 STWIN operated at 300 kV with 1 Å line resolution, having EDAX facility, to go forward.

Before SEM analysis the membrane samples were first frozen into liquid nitrogen and fractured cryogenically to analyze the cross-section. The SEM image of the membrane impregnated with Pt from diluted solution is showed in Fig. 2:

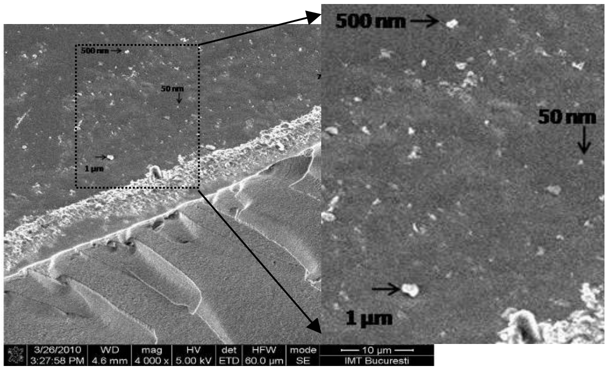

Fig. 2. SEM image of the nanocomposite membrane using 25 mM $NaBH_4$ reducing solution.

In this case the presence of no uniform platinum agglomerations on membrane surface is evidenced, covering a wide range of dimensions, from 50 nm to 1 μm, as it is showed in the SEM picture above.

In order to eliminate these defect sizes the concentration of $NaBH_4$ was increased, the new structure being presented in Fig. 3.

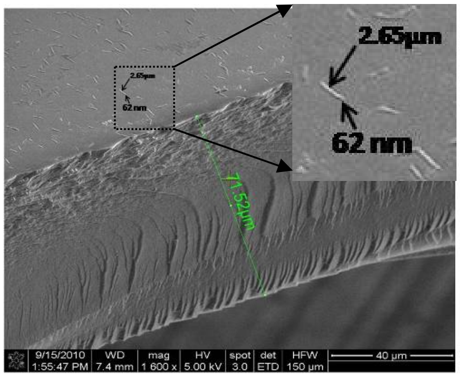

Fig. 3. SEM images of the nanocomposite membrane using 85 m M $NaBH_4$.

The image confirms that increasing of reducing agent concentration the dispersion of PtNPs on Nafion surface is improved, their dimensions being still large, with an acicular shape. Moreover, the cross section of the entire membrane evidences the thickness in its hydrated form. On the other hand, the presence of PtNPs inside of both types of membranes is not clear, being necessary further analyses using HR-TEM.

In order to make these analyses, the thin 50 nm cut slices of samples were prepared using a Leica EMUC6 Ultramicrotome. These slices were brought on a holey carbon coated copper grid. In this way there have been revealed PtNPs with 2-3.5 nm diameter, which might be can be attached or even got inside the sulphonic clusters of 4 nm from Nafion structure [30], as it is showed in Fig. 4a:

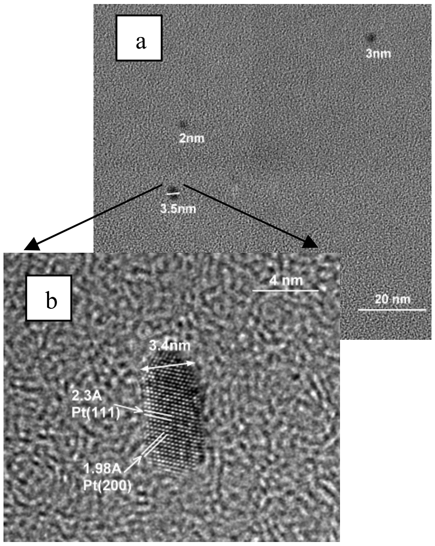

Fig. 4. TEM images of the first type of nanocomposite membrane (a) with detail for one NP (b).

The Fig. 4a reveals not so many platinum crystallites dispersed inside the Nafion membrane. Fig. 4b represents the detailed crystallite which is corresponding to (111) and (200) platinum lattices [31].

Complementary to HR-TEM characterization it were done compositional analysis of the obtained nanocomposite membrane using energy dispersive X-ray (EDAX). This type of characterization has been performed on several selected areas of samples taken from various preparation series and they confirm the presence of Pt particles on/inside the Nafion membrane subjected to impregnation process, the chemical composition being uniform and reproducible for a specific process flow (Fig. 5):

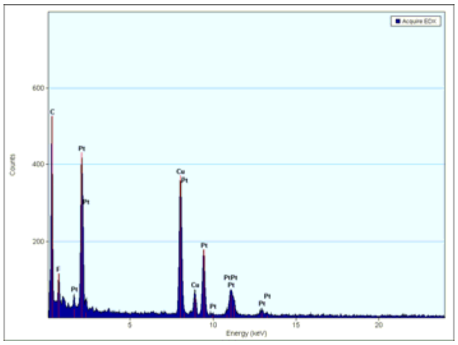

Fig. 5. EDAX analysis of the nanocomposite membrane.

The EDAX spectrum of the nanocomposite membrane clearly shows the Pt presence, next to other elements, like fluorine, carbon and oxygene. The presence of these is due to the Nafion based material, Teflon, while the presence of copper and part of carbon may be associated to the preparation sample protocol, as it is revealed in Fig. 6.

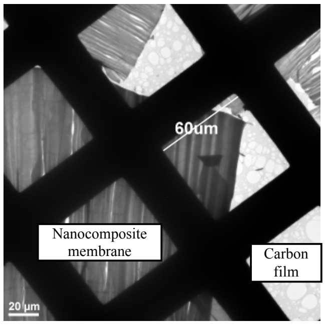

Fig. 6. Image of the sample preparation using copper grid.

In the case of increasing $NaBH_4$ concentration to 85 mM it was observed platinum polycristallites having dimensions of 27-23 nm, as it is showed in Fig. 7a.

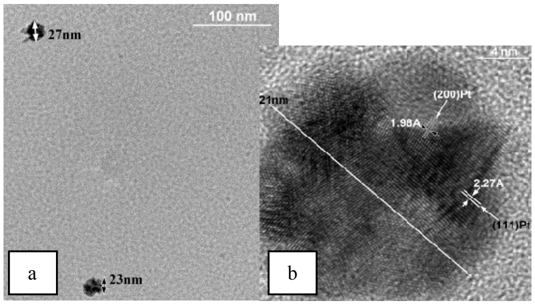

Fig. 7. TEM images of the second type of nanocomposite membrane: a- surface view, b- platinum polycrystallites detail.

Platinum polycristallites are arranged in some clusters corresponding to (111) and (200) platinum lattices also. In this case the compositional analysis is presented in Fig. 8, revealing the presence of platinum and also, of fluorine and oxygene.

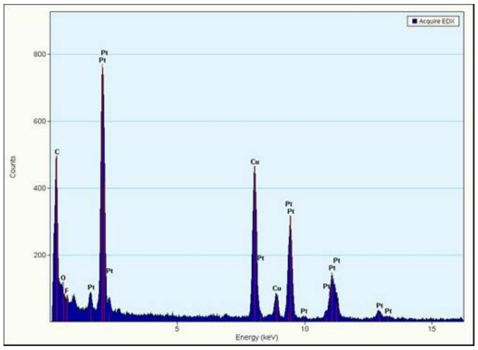

Fig. 8. EDAX analysis of the nanocomposite membrane obtained by increasing $NaBH_4$ concentration.

Comparing to Fig. 5, in this case it was obtained a bigger amount of platinum and the fluorine and carbon elements are decreasing.

The *surface area* (SA) of platinum nanoparticles is could be roughly estimated using formula:

$$SA = \frac{6 \times 1000}{21.4 \times d} \ (\mathrm{m^2 g^{-1}}) \tag{4}$$

where: *21.4* is the density of platinum nanoparticles (g cm^{-1}), and *d* is the mean particle size (nm).

In the case of using 25 mM $NaBH_4$ and taking into account that the mean size of platinum nanoparticles is 2.83 nm, the calculated surface area is 99.07 m^2g^{-1}. By increasing the reducing agent concentration, the *SA* of PtNPs became 62.31 m^2 g^{-1}.

3.2. X-ray diffraction investigation

The crystalline structure of the metallic nanostructures with respect of Nafion substrate was investigated by different X-ray diffraction methods using a Rigaku *SmartLab* thin film 9 kW rotating anode equipped with an in-plane arm θ-2θ angular scanning configuration with a Cu X-ray tube, a multilayer mirror (parallel beam, X-ray K_α wavelength $\lambda_{K\alpha}$= 1. 540609 Å) and an operating power of U= 40 kV, I= 40 mA, and a 2θ step of 0,05°; the contiguous X-ray emission spectra of the X-ray tube were filtered using a Ni absorber filter.

The XRD spectra of the starting protonated Nafion and the evolution after each of the experimental protocols are presented in Fig. 7:

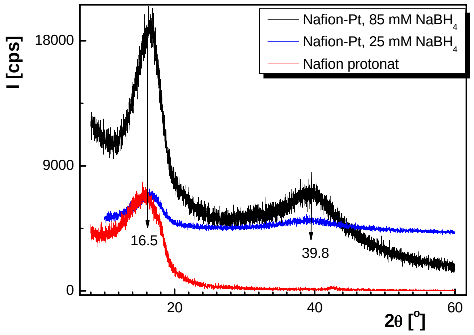

Fig. 9. XRD spectra of Nafion membrane before and after the PtNPs impregnation.

The Nafion spectrum reveals the amorphous structure of the membrane given by the 2θ peak from 16.5°. Regarding the nanocomposite structure, the intensity of this originar peak is lower in the case of nanocomposite membrane obtained using a smaller concentration of reducing agent, due to the transmission mode decided for the XRD measurements and also to the absorption determined by platinum impregnation. But, in the case of using a more concentrated solution of $NaBH_4$, the 2θ intensity peak from 16.5° is higher, maybe due to the bigger platinum amount or to the higher crystalinity degree of platinum. The 2θ intensity peak from 39.8° assigned to (111) platinum laticce is not intense in the first case, but in the second one, it is observed an intensity increasing; the Scherrer equation allows calculating the mean crystallite size [32]:

$$d = \frac{K\lambda}{\beta \cos\theta} \tag{5}$$

where d is the average of nanoparticles size (in Å), k – shape coefficient (0,9), λ – radiation wavelength (1.54056 Å), β – peak width (in radians) and θ – the corresponding Bragg angle for the peak maximum (in radians).

According to this formula, the mean crystallite size of the particles is 1.2 nm for the first case, and respectively 1,5 nm for the second one.

The small angle X-ray scattering (SAXS) technique is very precisely for analyzing small particles used to measure a wide range of nanoparticle sizes (from 1 to several tens of nanometers) [33] and the Fig. 10 presents the results of the experimental data fit with a spherically shaped particle model, since the ellipsoidal shaped model does not produce a good fit.

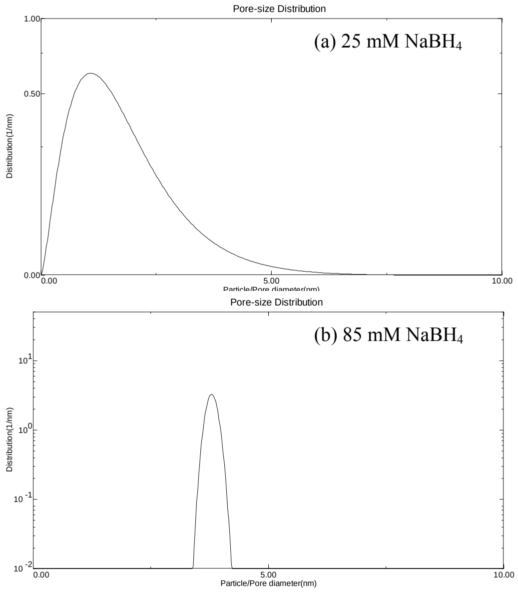

Fig. 10. Size distribution of Pt nanoparticles obtained from the SAXS pattern.

According to these SAXS measurements the PtNPs crystallite/polycrystallites dimensions are about 1.8 nm, respectively 3.8 nm, which are in good agreement with TEM results.

Other observation is related to the particles size distribution, which is broader in the case of using $NaBH_4$ solution of 25 mM. The Table 1 contains the summarized values obtained using two complementary techniques for particle sizes characterization.

Table 1. Platinum nanoparticle size dimensions obtained using TEM and SAXS techniques.

$NaBH_4$ concentration (mM)	PtNP dimensions / characterization technique (nm)	
	TEM	SAXS
25	2	1.8
85	4.5	3.8

As can be seen, there is a good correlation between the results obtained using two methods of analysis, the lower values given by XRD representing the crystalline core of the NPs.

4. Conclusions

The fabrication of nanocomposite mebrane based on platinum nanoparticles is reported here. The method used was *in situ* one, by alcoholic reduction of the chloroplatinic acid inside the Nafion membrane, using as reducing agent, sodium borohydride, with two types of concentration, in order to see if there is any influence over nanoparticles formation. The obtained nanocomposite structure was analyzed using electronic microscopy techniques, SEM and HR-TEM, and also by XRD, to see the microphase structure.

The results show a good correlation between the XRD and HR-TEM analyzing methods. Using a more concentrated solution of reducing agent gives rise to clusters of polycrystallites platinum with an increased average diameter and regular shape. Also these particles have a better distribution inside and even on the Nafion membrane.

The results open the possibility to use platinum nanoparticles dispersed in Nafion membrane to measure the conductivity of this new type on nanocomposite membrane, as application for proton exchange membrane in direct methanol fuel cells.

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References

[1] T. E. Springer, T. A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc., **138**, 2334 (1991).
[2] X. Ren, T. E. Springer, S. Gottesfeld, J. Electrochem. Soc., **147**, 92 (2000).
[3] E. A. Ticianelli, C. R. Derouin, A. Redondo, S. Srinivasan, J. Electrochem. Soc., **135**, 2209 (1988).
[4] J. A. Kerres, J. Membr. Sci., **185**, 3 (2001).
[5] K. D. Kreuer, J. Membr. Sci., **185**, 29 (2001).
[6] K. A. Mauritz, R. E. Moore, Chem. Rev. **104**, 4535 (2004).
[7] H. L. Yeager, A. Steck. J. Electrochem. Soc. **128**, 1880 (1981).
[8] T. D. Gierke, G. E. Munn, F. C. Wilson, J. Polym. Sci.: Polym. Phys. Ed. **19**, 1687 (1981).
[9] W. Y. Hsu, T. D. Gierke, Macromolecules **15**, 101 (1982).
[10] K. Adjemian, S. Lee, S. Srinivasan, A. Bocarsly, J. Benziger, J. Electrochem. Soc., **149**, A256 (2002).
[11] V. Ramani, H. R. Kunz, J. M. Fenton, J. Membr. Sci. **266**, 110 (2005).
[12] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, J. Membr. Sci. **185**, 73 (2001).
[13] P. Jannasch, Curr. Opin. Colloid Interface Sci. **8**, 96 (2003).
[14] G. Alberti, M. Casciola, Annu. Rev. Mater. Res. **33**, 129 (2003).
[15] D. J. Jones J. Rozière, Annu. Rev. Mater. Res., 33 (2003).

[16] Q. Li, R. He, R. Berg, H. A. Hjuler, N. J. Bjerrum, Solid State Ionics **168**, 177 (2004).

[17] L. Xiao, H. Zhang, E. Scanlon, L. S. Ramanathan, E. W. Choe, D. Rogers, T. Apple, B. C. Benicewicz, Chem. Mater. **17**, 5328 (2005).

[18] C. Yang, S. Srinivasan, A. S. Arico, P. Creti, V. Baglio, V. Antonucci, Electrochem. Solid State Lett. **4**, A31 (2001).

[19] T. A. Zawodzinski, Jr., C. Derouin, S. Radzinski, R. J. Sherman, V. T. Smith, T. E. Springer, S. Gottesfeld, J. Electrochem. Soc. **140**, 1041 (1993).

[20] Q. Deng, R. B. Moore K. A. Mauritz, J. Appl. Polym. Sci. **68**, 747 (1998).

[21] H. L. Tang, M. Pan, S. P. Jiang, R. Z. Yuan, Mater. Lett. **59**, 376 (2005).

[22] H. Uchida, Y. Mizuno, M.Watanabe, J. Electrochem. Soc. **149**, A682 (2002).

[23] A. W. H. Mau, C. B. Huang, N. Kakuta, A. J. Bard, A. Campion, M. A. Fox, J. M. White, S. E. Webber, J. Am. Chem. Soc. **106**, 6537 (1984).

[24] Z. Liu, Z. Q. Tian, S. P. Jiang, Electrchim. Acta, **56**, 1213 (2006).

[25] H. Zhang, Y. Guo, L. Wan, C. Bai, Chem. Commun. **24**, 3022 (2003).

[26] S. Duron, R. Rivera-Noriega, P. Nkeng, G. Poillerat, O. Solorza-Feria, J. Electroanal. Chem. **566**, 281 (2004).

[27] A. J. Dickinson, L. P. L. Carrette, J. A. Collins, K. A. Friedrich, U. Stimming, Electrochim. Acta **47**, 3733 (2002).

[28] S. N. Pronkin, G. A. Tsirlina, O. A. Petrii, S. Y. Vassiliev, Electrochim. Acta **46**, 2343 (2001).

[29] Z. Liu, J. Y. Lee, M. Han, W. Chen, L. M. Gan, J. Mater. Chem. **12**, 2453 (2002).

[30] C. Heitner-Wirguin. Journal of Membrane Science **120**, 1 (1996).

[31] P. C. Lee, D. Ouk Kim, T. H. Han, S. J. Kang, L. Sun Pu, J. D. Nam, Macromolecular Research, **17**(3), 187 (2009).

[32] P. Scherrer, Göttinger Nachr **2**, 98 (1918).

[33] H. Song, R. M. Rioux, J. D. Hoefelmeyer, R. Komor, K. Niesz, M. Grass, P. Yang, G. A. Somorjai, J. Am. Chem. Soc. **128**, 3027 (2006).

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